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EP 0633496 A

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(54) **Photographic material with antistatic layer**

(57) A multilayer silver halide photographic material is provided having an outermost hydrophilic colloid antistatic layer comprising a combination of an anionic surface active agent and a cationic surface active agent wherein at least one of said agents comprises at least one polyoxyalkylene group, said combination being present in an amount to provide from 0.05 to 0.2 g/m² dry coverage, and wherein a layer adjacent the outermost layer contains a dye, preferably an antihalation dye.

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Photographic Material

Field of the Invention

The invention relates to photographic materials.

Background of the Invention

5 Multilayer silver halide photographic materials
having an outermost hydrophilic colloid layer comprising
a plurality of surface active agents which provide
antistatic properties are known. Examples of such
compositions are shown in US-A-4 891 307 in which the
10 surface active agent combination includes a nonionic
surface active agent comprising a polyoxyalkylene group.

Co-pending European Patent Application No.
94202730.1 describes an antistatic composition for use in
photographic materials which comprises a combination of
15 an anionic surface active agent and a cationic surface
active agent wherein at least one of the agents comprises
at least one polyoxyalkylene group. Use of the
composition in the pelloid layer of a photographic
material containing an antihalation dye is described.
20 The amount of the surfactant combination taught provides
a dry coverage in the outermost layer of 0.45 to 0.91
g/m².

Problem to be solved by the Invention

Use of a combination of an anionic surface active
25 agent and a cationic surface active agent wherein at
least one of the agents comprises at least one
polyoxyalkylene group in a dye-containing pelloid layer
in an amount of 0.45g/m² or more can result in dye stain
in the processed material.

Summary of the Invention

30 The invention provides a multilayer silver
halide photographic material having an outermost
hydrophilic colloid layer comprising a plurality of
surface active agents characterised in that the surface
35 active agents comprise a combination of an anionic

surface active agent and a cationic surface active agent wherein at least one of said agents comprises at least one polyoxyalkylene group, said combination being present in an amount to provide from 0.05 to 0.2 g/m² dry coverage, and wherein a layer adjacent the outermost layer contains a dye.

Advantageous Effect of the Invention

The surfactant combination provides adequate antistatic protection before processing and dye stain is avoided in the processed material.

Detailed Description of the Invention

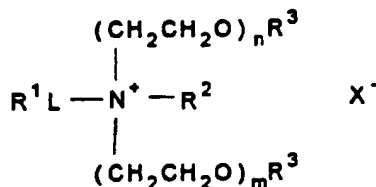
A preferred hydrophilic colloid is gelatin e.g. alkali-treated gelatin (cattle bone or hide gelatin) and acid-treated gelatin (pigskin gelatin) or a gelatin derivative e.g. acetylated gelatin and phthalated gelatin. Other suitable hydrophilic colloids include naturally occurring substances such as proteins, protein derivatives, cellulose derivatives e.g. cellulose esters, polysaccharides e.g. dextran, gum arabic, zein, casein and pectin, collagen derivatives, agar-agar, arrowroot and albumin. Examples of suitable synthetic hydrophilic colloids include polyvinyl alcohol, acrylamide polymers, maleic acid copolymers, acrylic acid copolymers, methacrylic acid copolymers and polyalkylene oxides.

Suitable surface active agents may be chosen from any known surface active agents.

Examples of cationic surface active agents are as follows.

1. N-ethoxylated long chain ammonium salts including quaternised ethoxylated amines and non-ethoxylated equivalents.

These compounds are represented by general structure I:



wherein

R^1 is an alkyl, alkenyl, alkylaryl or arylalkyl chain having from 8 to 20 carbon atoms or a partially or fully fluorinated alkyl, alkenyl, alkylaryl or arylalkyl chain of equivalent hydrophobic strength e.g. having from 4-14 carbon atoms;

R^2 is hydrogen, methyl or benzyl;

R^3 is hydrogen or methyl (preferably R^3 is hydrogen if the sum of n and m is greater than 0;

X^- is halide (preferably Br^- or Cl^-);

L represents a suitable linking chemistry between R^1 and the positively charged nitrogen e.g. a covalent chemical bond or $-(\text{CH}_2\text{CH}_2\text{O})_x-$;

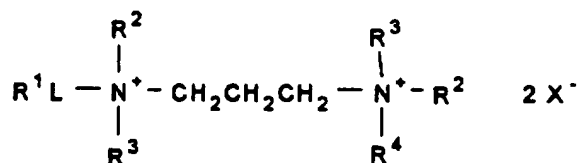
each m and n independently is 0 or an integer from 1 to 20; and,

x is an integer from 1 to 20.

Examples of such materials wherein R^1 is alkyl or alkenyl derived from natural oils, R^2 is methyl and R^3 is hydrogen are EthoquadTM C/12, C/25, O/12 and HT/25 surfactants manufactured by Akzo Chemie, wherein the sum of n and m is 2, 15, 2 and 15, respectively, (see Trade Literature for detailed structures). Simple quaternary ammonium compounds wherein the sum of n and m is 0, R^1 is alkyl, R^2 is methyl or benzyl and R^3 is methyl (i.e. alkyltrimethylammonium or alkyl dimethylbenzylammonium halides) are readily available, e.g. ArquadTM surfactants manufactured by Akzo Chemie, and can be used in cases where the degree of ethoxylation associated with the anion is sufficient to make the resulting complex water soluble or dispersible.

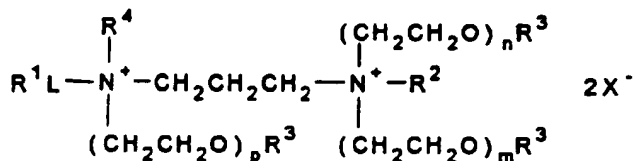
2. Dication surfactants of general structure

II.



wherein R¹ is an alkyl, alkenyl, alkylaryl or arylalkyl
chain having from 8 to 20 carbon atoms and each of R², R³
and R⁴ independently is an alkyl group having from 1 to 4
carbon atoms. An example of such a compound which is
commercially available is DuoquadTM manufactured by Akzo
Chemie, wherein R¹ is predominantly C₁₂ alkyl based on
coconut oil and R², R³ and R⁴ are each methyl.

3. Examples of compound I, wherein R² and R³
are hydrogen, can be made from EthomeensTM
(ethoxylated amines manufactured by Akzo Chemie) by
simply reacting the EthomeenTM with the appropriate
hydrogen halide. Corresponding dicationic structures can
be made from EthoduomeensTM (ethoxylated diamines
manufactured by Akzo Chemie). Quaternised derivatives
can also be made. These dicationic compounds
are represented by the general structure III:



wherein

R¹ is an alkyl, alkenyl, alkylaryl or arylalkyl
chain having from 8 to 20 carbon atoms;

R² is hydrogen, methyl or benzyl;

each R³ independently is hydrogen or methyl;

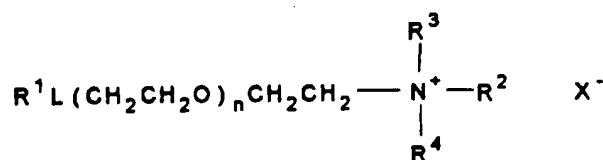
R⁴ is an alkyl group having from 1 to 4 carbon
atoms or benzyl;

X is halide e.g. chloride or bromide; and,

each of m, n and p is 0 or an integer from 1 to 15.

Preferably, R³ is hydrogen if the sum of m and n is greater than 0.

- 5 4. Ammonium salts of amine derivatives of an ethoxylated long chain hydrocarbon or fluorocarbon alcohol including the quaternary ammonium product having the general structure IV:



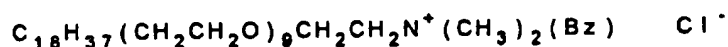
10 wherein

R¹ is an alkyl, alkenyl, alkylaryl or arylalkyl chain having from 8 to 20 carbon atoms;

- 15 each of R², R³ and R⁴ independently is an alkyl group having from 1 to 4 carbon atoms or benzyl provided that if R², R³ or R⁴ is benzyl, the other two groups are not benzyl;

X is halide e.g. chloride or bromide; and, n is an integer from 1 to 30 .

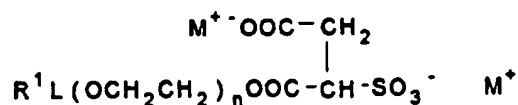
- 20 A specific example of a compound of structure IV is



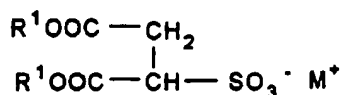
wherein Bz is benzyl.

Examples of anionic surface active agents are as follows.

- 25 1. Sulphosuccinates having the general structure V(a):



or V(b):



wherein

each R^1 independently is an alkyl, alkenyl, alkylaryl or arylalkyl chain having from 8 to 20 carbon atoms;

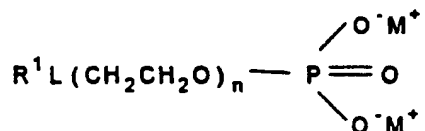
M^+ is a suitable monovalent cation e.g. an alkali metal cation such as Na^+ , K^+ , Li^+ ; ammonium; alkylammonium such as $\text{N}(\text{CH}_3)_4^+$, $\text{N}(\text{C}_2\text{H}_5)_4^+$ and $\text{N}(\text{C}_3\text{H}_7)_4^+$; and,

n is an integer from 1 to 30.

Examples of compounds having structure V(a) are: AerosolTM 102 (Cyanamid; $n = 5$, $L =$ covalent bond, $\text{R}^1 =$ a C_{10} - C_{12} straight chain alkyl group); SermulTM EA176 (Servo BV; $n = 10$, $L =$ covalent bond, $\text{R}^1 =$ nonylphenyl).

Examples of compounds having structure V(b) are: AerosolTM MA (Cyanamid; $\text{R}^1 =$ hexyl); and the compound described in US A-4 968 599 ($\text{R}^1 = n\text{-C}_3\text{F}_7\text{CH}_2$).

2. Phosphates having the general structure VI:



wherein

R^1 is an alkyl, alkenyl, alkylaryl or arylalkyl chain having from 8 to 20 carbon atoms;

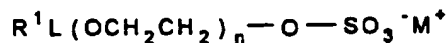
L is a simple linking group such as $-\text{O}-$ or a covalent bond;

M^+ is a suitable monovalent cation e.g. an alkali metal cation such as Na^+ , K^+ , Li^+ ; ammonium; alkylammonium such as $\text{N}(\text{CH}_3)_4^+$, $\text{N}(\text{C}_2\text{H}_5)_4^+$ and $\text{N}(\text{C}_3\text{H}_7)_4^+$; and,

n is an integer from 1 to 30.

Examples of compounds having structure VI are: SermulTM surfactants EA211, EA188, and EA205 (Servo BV, R¹ = nonylphenyl, L = -O-, M⁺ = Na⁺, and n = 6, 10, and 50, respectively).

- 5 3. Sulphates having the general structure VII:



wherein

R¹ is an alkyl, alkenyl, alkylaryl or arylalkyl chain having from 8 to 20 carbon atoms or a fluoroalkyl group having 4 to 14 carbon atoms

L is a simple linking group such as -O- or a covalent bond;

M⁺ is a suitable monovalent cation e.g. an alkali metal cation such as Na⁺, K⁺, Li⁺; ammonium; alkylammonium such as N(CH₃)₄⁺, N(C₂H₅)₄⁺ and N(C₃H₇)₄⁺; and,

n is 0 or an integer from 1 to 30.

Examples of compounds having structure VII are: sodium dodecyl sulphate (R¹ = dodecyl, n = 0); SermulTM surfactants EA54, EA151, EA146 (Servo BV, R¹ = nonylphenyl, L = covalent bond, M⁺ = Na⁺ and n = 4, 10, and 15, respectively); PolystepTM B23 (Stepan, R¹ = dodecyl, and n = 10); sulphated derivatives of BrijTM 76 and 78 (ICI, R¹ = C₁₈H₃₇ (average), L = covalent bond, and n = 10 and 20, respectively).

4. Sulphonates having the general structure VIII:



wherein

R¹ is an alkyl, alkenyl, alkylaryl or arylalkyl chain having from 8 to 20 carbon atoms;

L is a simple linking group such as -O- or a covalent bond;

M is a suitable monovalent cation e.g. an alkali metal cation such as Na^+ , K^+ , Li^+ ; ammonium; alkylammonium such as $\text{N}(\text{CH}_3)_4^+$, $\text{N}(\text{C}_2\text{H}_5)_4^+$ and $\text{N}(\text{C}_3\text{H}_7)_4^+$; and,

5 n is 0 or an integer from 1 to 30.

Examples of compounds having structure VIII are: TritonTM X-200 (Rohm and Haas, $\text{R}^1 = t\text{-octylphenyl}$, L = covalent bond, n = 2-4 nominal and $\text{M}^+ = \text{Na}^+$); FT248TM (Bayer, $\text{R}^1 = \text{perfluorooctyl}$, L = covalent bond, n = 0 and
10 $\text{M}^+ = \text{N}(\text{C}_2\text{H}_5)_4^+$).

5. Fluorocarboxylates having the general structure IX:



15 wherein

R^1 is a fluoroalkyl chain having from 6 to 9 carbon atoms e.g. C_7F_{15} , C_8F_{17} and C_9F_{19} ; and,

M^+ is a suitable monovalent cation e.g. an alkali metal cation such as Na^+ , K^+ , Li^+ ; ammonium;
20 alkylammonium such as $\text{N}(\text{CH}_3)_4^+$, $\text{N}(\text{C}_2\text{H}_5)_4^+$ and $\text{N}(\text{C}_3\text{H}_7)_4^+$.

Preferably, the combination of cationic surface active agent and anionic surface active agent is present in an amount from 0.5 to 5, more preferably from 2 to 3 percent, by weight based on the wet laydown of the
25 supercoat or outermost layer which is coated to provide from 0.05 to 0.2, preferably from 0.1 to 0.15, g/m^2 dry coverage.

The molar ratio of cationic to anionic surface active agent is preferably from 1:2 to 2:1, most
30 preferably 1:1.

Preferably, both cationic and anionic surface active agents comprise at least one polyoxyalkylene group.

The mixture of surface active agents imparts low surface electrical resistivity e.g. 10^{10} to 10^{11} ohms/square, 50%RH/20°C to dried aqueous gelatin coatings.

5 The complex formed between the cationic and anionic surface active agents is preferably water soluble or sufficiently water dispersible so as not to deleteriously affect coating. In fact, the surface active agents may also act as coating aids.

10 Optionally, other materials may be present in the outermost layer if appropriate to enhance coating uniformity and/or surface conductivity properties, e.g. other nonionic surfactants, a low lattice energy salt such as lithium trifluoromethane-sulphonate (triflate),
15 and a matting agent to increase surface roughness and reduce surface contact.

The outermost layer is free of any dye which would cause dye stain after processing.

20 A dye-containing layer, e.g. another hydrophilic colloid layer, is present adjacent the outermost layer. Examples of dyes which may be contained in the layer include antihalation dyes and sensitizing dyes.

Preferably, the dyes are acid group-containing dyes or the salts thereof.

25 The invention is applicable to a variety of photographic materials. A specific example of the use of the invention is in a two layer pelloid coating for a graphic arts film.

30 In the following discussion of suitable materials for use in the photographic element according to the invention, reference will be made to *Research Disclosure*, December 1989, Item 308119, published by Kenneth Mason Publications Ltd., Emsworth, Hampshire PO10 7DQ, U.K., the disclosures of which are incorporated in

their entireties herein by reference. This publication will be identified hereafter as "Research Disclosure".

The support of the element of the invention can be any of a number of well known supports for
5 photographic elements. These include polymeric films, such as cellulose esters (for example, cellulose triacetate and diacetate) and polyesters of dibasic aromatic carboxylic acids with divalent alcohols (such as polyethylene terephthalate), paper, and polymer-coated
10 paper.

The photographic elements according to the invention can be coated on the selected supports as described in Research Disclosure Section XVII and the references cited therein.

15 The radiation-sensitive layer of a photographic element according to the invention can contain any of the known radiation-sensitive materials, such as silver halide, or other light sensitive silver salts. Silver halide is preferred as a radiation-sensitive material.
20 Silver halide emulsions can contain for example, silver bromide, silver chloride, silver iodide, silver chlorobromide, silver chloriodide, silver bromiodide, or mixtures thereof. The emulsions can include coarse, medium, or fine silver halide grains bounded by 100, 111,
25 or 110 crystal planes.

The silver halide emulsions employed in the elements according to the invention can be either negative-working or positive-working. Suitable emulsions and their preparation are described in Research
30 Disclosure Sections I and II and the publications cited therein.

Also useful are tabular grain silver halide emulsions. In general, tabular grain emulsions are those in which greater than 50 percent of the total grain
35 projected area comprises tabular grain silver halide

crystals having a grain diameter and thickness selected so that the diameter divided by the mathematical square of the thickness is greater than 25, characterized in that the diameter and thickness are both measured in
5 microns. An example of tabular grain emulsions is described in U.S. Patent No. 4,439,520.

Suitable vehicles for the emulsion layers and other layers of elements according to the invention are described in Research Disclosure Section IX and the
10 publications cited therein.

The radiation-sensitive materials described above can be sensitized to a particular wavelength range of radiation, such as the red, blue, or green portions of the visible spectrum, or to other wavelength ranges, such
15 as ultraviolet, infrared, X-ray, and the like. Sensitization of silver halide can be accomplished with chemical sensitizers such as gold compounds, iridium compounds, or other group VIII metal compounds, or with spectral sensitizing dyes such as cyanine dyes,
20 merocyanine dyes, or other known spectral sensitizers. Exemplary sensitizers are described in Research Disclosure Section IV and the publications cited therein.

Multicolor photographic elements according to the invention generally comprise a blue-sensitive silver
25 halide layer having a yellow color-forming coupler associated therewith, a green-sensitive layer having a magenta color-forming coupler associated therewith, and a red-sensitive silver halide layer having a cyan color-forming coupler associated therewith.

30 The elements according to the invention can include couplers as described in Research Disclosure Section VII, paragraphs D, E, F and G and the publications cited therein. These couplers can be incorporated in the elements and emulsions as described

in Research Disclosure Section VII, paragraph C and the publications cited therein.

A photographic element according to the invention, or individual layers thereof, can also include
5 any of a number of other well-known additives and layers. These include, for example, optical brighteners (see Research Disclosure Section V), antifoggants and image stabilizers (see Research Disclosure Section VI), light-absorbing materials such as filter layers of intergrain
10 absorbers, and light-scattering materials (see Research Disclosure Section VIII), gelatin hardeners (see Research Disclosure Section X), oxidized developer scavengers, coating aids and various surfactants, overcoat layers, interlayers, barrier layers and antihalation layers (see
15 Research Disclosure Section VII, paragraph K), antistatic agents (see Research Disclosure Section XIII), plasticizers and lubricants (see Research Disclosure Section XII), matting agents (see Research Disclosure Section XVI), antistain agents and image dye stabilizers
20 (see Research Disclosure Section VII, paragraphs I and J), development-inhibitor releasing couplers and bleach accelerator-releasing couplers (see Research Disclosure Section VII, paragraph F), development modifiers (see Research Disclosure Section XXI), and other additives and
25 layers known in the art.

Photographic elements according to the invention can be exposed to actinic radiation to form a latent image as described in Research Disclosure Section XVIII. The photographic elements can be processed to
30 form an image by a process appropriate to the structure and intended function of the particular element. Such processes include those which produce silver images, either negative images or direct positive images. Such processes include those typically used for black and
35 white negative film and silver prints, medical X-ray

materials, and materials used in graphic arts and lithographic applications. Processes can be used which produce dye images. These include, but are not limited to, the C-41, E-6, RA-4, EP-2, ECN-2 and ECP-2A processes of the Eastman Kodak Company. Useful processes which produce dye images can produce negative or positive color images, or can produce monochrome dye images.

The invention is further illustrated by the following examples, without being limited thereby.

10 EXPERIMENTAL METHODS USED

1. Determination of Electrostatic Properties

To determine the electrostatic properties of the materials described in this invention the following sequence was employed:

- 15 i) The materials were coated in an aqueous gelatin composition by machine;
 - ii) The coatings were dried;
 - iii) The coatings were conditioned at constant RH (15% and 50%) for at least four hours;
- 20 iv) The surface electrical resistivity was measured under constant RH using simple bar electrodes and suitable electrometer.
- v) Coatings were processed through a commercial graphic arts photographic processor, an "Interpro 20RA" (IGP (UK) Ltd), and then measured for surface electrical resistivity following the procedure from ii) to iv).

2. Machine Coating

A typical pelloid layer of the type employed in graphic arts photographic products was used as a vehicle for the coating studies. Pelloid layers are generally coated on the back surface of a photographic material to impart a variety of features to the final product. Examples of possible functions of a pelloid layer are:

- 35 i) Antihalation;

- ii) Curl control;
- iii) Safelight protection;
- iv) Matte;
- v) Front-to-back recognition;
- 5 vi) Antistatic.

In the context of this invention it is the last feature that is being addressed.

Table 1: Pelloid Coating - Layer 1 (Underlayer)

| Component | Amount | Composition of Component |
|-------------------|------------------------------|---|
| Dry gelatin | 77.4g | As component |
| Deionised water | 819.5g | As component |
| 2N Sulphuric acid | 5.9ml | As component |
| Solution of Dye A | 21.7ml | Solution Dye A = 298g of Dye A/litre (also contains 24ml/litre 2N propionic acid) |
| Solution of Dye B | 18.1ml | Solution Dye B = 207g of Dye B/litre (also contains 5ml/litre 2.5N NaOH) |
| Solution of Dye C | 52.9ml | Solution Dye C = 20.3g of Dye C/litre (also contains 68ml/litre of an ammonia solution containing 96ml of "890" ammonia/kg of solution) |
| Solution of Dye D | 4.5ml | Solution Dye D = 169g of Dye D/litre |
| Hardener solution | 224.8ml | 18g of bis(vinylsulphonyl) methane/litre (also contains 10ml/litre 2.18M KNO ₃) |
| Deionised water | To make 1000g total solution | As component |

The above underlayer was coated at 16m/min coating speed, at 40°C, at a coverage of 46.7ml/m² onto 5 inch wide by 0.004 inch thick polyethylene-terephthalate film base suitably subbed to give good adhesion to gelatin-based coated layers. Coated simultaneously above the underlayer was a second, supercoat, layer at a coverage of 4.8ml/m².

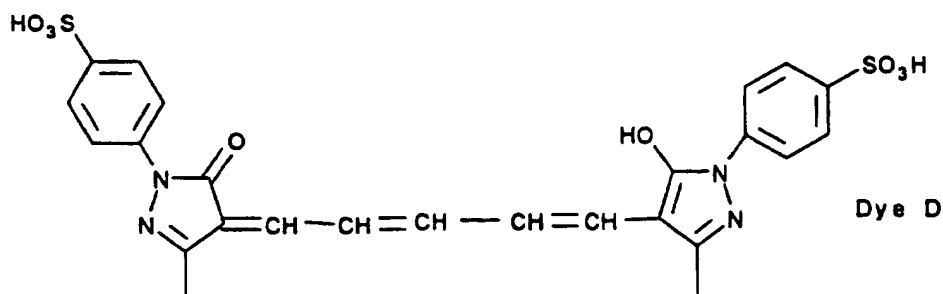
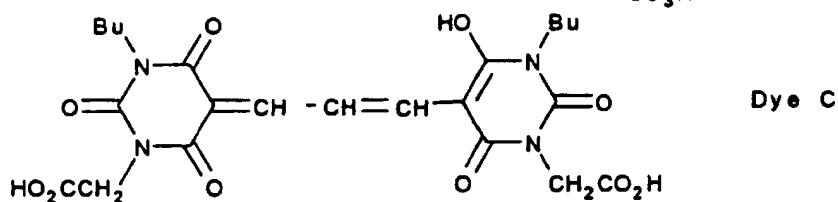
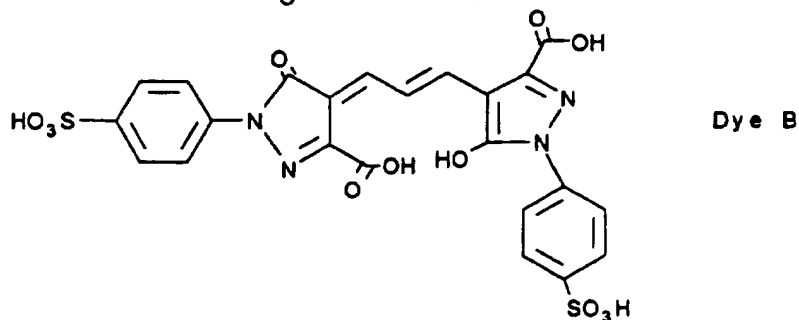
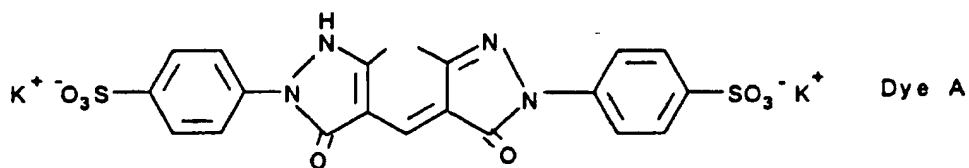


Table 2: Pelloid Coating - Layer 2 (Supercoat)

| Component | Amount | Composition of Component |
|---|------------------------------|--|
| Dry gelatin | 96.9g | As component |
| Deionised water | 378.3g | As component |
| Matting bead dispersion | 118g | 7.8% matting beads, 5% gelatin |
| 2N Sulphuric acid | 7.1ml | As component |
| Water + surfactant solutions + low lattice energy salt (optional) | To make 1000g total solution | According to concentrations required of surfactant and low lattice energy salt |

Example

- 5 The surface resistivity before processing and after processing a number of pelloid coatings containing different combinations of cationic and anionic surfactants in accordance with the invention is given in Table 3.

10

Table 3: Surface electrical resistivity behaviour of coatings containing specified surfactant combinations

| Cationic Surfactant | Anionic Surfactant | Total wt. % (supercoat wt. %) surfactant complex | Total wt. % (Supercoat wt. %) CF ₃ SO ₃ Li | Log R 50% RH (15% RH) Before Processing | Log R 50% RH (15% RH) After Processing |
|---------------------|--------------------|--|--|--|---|
| Ethoquad HT/25 | Triton X-200 | 0.24 (2.6) | - (-) | 10.9 (13.2) | 11.85 (14.0) |
| Ethoquad HT/25 | Triton X-200 | 0.24 (2.6) | 0.12 (1.3) | 10.6 (12.2) | 11.9 (13.9) |
| Ethoquad HT/25 | Sermul EA211 | 0.24 (2.6) | - (-) | 11.2 (11.2) | 12.5 (14.5) |
| Ethoquad HT/25 | Sermul EA211 | 0.24 (2.6) | 0.12 (1.3) | 10.6 (10.8) | 12.4 (13.9) |
| Ethoquad HT/25 | Sermul EA146 | 0.24 (2.6) | - (-) | 11.0 (12.6) | 12.1 (13.9) |
| Ethoquad HT/25 | Sermul EA146 | 0.24 (2.6) | 0.12 (1.3) | 10.5 (10.5) | 12.0 (13.9) |

Note: R denotes surface electrical resistivity measured in ohms/square at 20°C.

The surfactant level used is equivalent to 0.125g/m² dry coverage.

The triflate level, when used, is equivalent to 0.062g/m² dry coverage.

The table shows that the combination of cationic and anionic surfactants have imparted a low surface electrical resistivity to the coatings before processing. The figures obtained at 50% RH are between 10.5 and 11.2 log ohms/square, in line with the figure of ~11 log ohms/square or less required to prevent charging of a film in contact with a roller at a velocity of 10cm/sec.

In the three combinations quoted the presence of the low lattice energy salt (triflate) lowers the surface electrical resistivity of the unprocessed coatings at both 50 and 15% RH.

No advantage is seen after processing. At very low (15%) RH static protection is still offered by certain combinations of surfactant and triflate.

5 These data are compared to coatings containing the non process surviving surfactant antistat of the prior art (Zonyl FSN) and to coatings containing a surfactant combination (Olin 10G + Triton X-200) which does not give antistatic properties (Table 4).

10 **Table 4: Surface electrical resistivity behaviour of coatings containing surfactants of the prior art**

| Surfactants | Total wt.% (supercoat wt.%) surfactants | Total wt.% (Supercoat wt.%) CF ₃ SO ₂ Li | Log R 50% RH (15% RH Before Processing | Log R 50% RH (15% RH) After Processing |
|--|---|---|--|--|
| Zonyl FSN + Olin 10G mixed 1:4.18 respectively | 0.083 (0.89) [dry coverage = 0.043g/m ²] | 0.14 (1.5) [dry coverage = 0.072g/m] | 11.4 (12.5) | 13.2 (14.9) |
| Zonyl FSN | 0.24 (2.6) [dry coverage = 0.125g/m ²] | 0.12 (1.3) [dry coverage = 0.062g/m ²] | 10.3 (10.8) | 12.6 (14.3) |
| Triton X-200 + Olin 10G mixed 1:1.76 respectively | 0.033 (0.35) [dry coverage = 0.017g/m ²] | - (-) | 12.5 (14.55) | 13.7 (15.0) |
| Triton X-200 + Olin 10G mixed 1:1.76 respectively | 0.24 (2.6) [dry coverage = 0.125g/m ²] | - (-) | 11.8 (14.5) | 13.2 (15.0) |

Note: R denotes surface electrical resistivity measured in ohms/square at 20°C

15 The lack of dye stain on processed samples is illustrated in Table 5 which records the base-corrected transmission densities of coatings as measured by a "X-Rite 310"

photographic densitometer. Values for the visual, red, green and blue channels are quoted. It can be seen that in all cases the densities of all samples are <0.01, indicating negligible retention of any of the four typical pelloid dyes used during the illustration of the invention.

Table 5: Transmission densities of processed coatings containing specified surfactant combinations

| Cationic Surfactant | Anionic Surfactant | Total wt. % (supercoat wt. %) surfactant complex | Total wt. % (Supercoat wt. %) CF ₃ SO ₃ Li | DT Vis | DT Red | DT Grn | DT Blue |
|---------------------|--------------------|--|--|-----------|-----------|-----------|------------|
| Ethoquad HT/25 | Triton X-200 | 0.24 (2.6) | - (-) | 0.006 | 0.002 | -0.001 | 0.000 |
| Ethoquad HT/25 | Triton X-200 | 0.24 (2.6) | 0.12 (1.3) | 0.006 | 0.001 | -0.001 | 0.000 |
| Ethoquad HT/25 | Sermul EA211 | 0.24 (2.6) | - (-) | 0.007 | 0.005 | 0.000 | 0.002 |
| Ethoquad HT/25 | Sermul EA211 | 0.24 (2.6) | 0.12 (1.3) | 0.007 | 0.003 | 0.000 | 0.003 |
| Ethoquad HT/25 | Sermul EA146 | 0.24 (2.6) | - (-) | 0.004 | 0.001 | -0.001 | 0.000 |
| Ethoquad HT/25 | Sermul EA146 | 0.24 (2.6) | 0.12 (1.3) | 0.006 | 0.001 | -0.001 | 0.000 |

Note: DT denotes base-corrected transmission density

The coatings shown in Table 6 illustrate that higher concentrations of surfactant give problems with dye stain. Compared to those shown in Table 5, the level of surfactant in the supercoat remains unchanged. However, as a percentage of the total wet laydown a figure of 2.1% is illustrated, achieved by including surfactant within the underlayer melt (see Table 1).

Table 6: Transmission densities of processed coatings containing specified surfactant combinations present in both surpercoat and underlayer

| Cationic Surfactant | Anionic Surfactant | Total wt. % (supercoat wt. %) surfactant complex | Total wt. % (Supercoat wt. %) CF ₃ SO ₃ Li | DT Vis | DT Red | DT Grn | DT Blue |
|---------------------|--------------------|--|--|--------|--------|--------|---------|
| Ethoquad HT/25 | Triton X-200 | 2.1 (2.6) | - (-) | 0.042 | 0.056 | 0.023 | 0.037 |
| Ethoquad HT/25 | Triton X-200 | 2.1 (2.6) | 1.05 (1.3) | 0.031 | 0.039 | 0.015 | 0.034 |
| Ethoquad HT/25 | Sermul EA211 | 2.1 (2.6) | - (-) | 0.054 | 0.077 | 0.033 | 0.084 |
| Ethoquad HT/25 | Sermul EA211 | 2.1 (2.6) | 1.05 (1.3) | 0.037 | 0.048 | 0.024 | 0.079 |
| Ethoquad HT/25 | Sermul EA146 | 2.1 (2.6) | - (-) | 0.028 | 0.036 | 0.015 | 0.021 |
| Ethoquad HT/25 | Sermul EA146 | 2.1 (2.6) | 1.05 (1.3) | 0.025 | 0.031 | 0.012 | 0.023 |

5 Note: DT denotes base-corrected transmission density

The surfactant level used is equivalent to 1.10g/m² dry coverage

The triflate level, when used, is equivalent to 0.55g/m² dry coverage

10 It can be seen that visual transmission densities between 0.025 and 0.054 are given, depending on the exact surfactant combination. This level of retained dye would be unacceptable in a commercially produced material, despite the fact that these particular combinations do impart antistatic protection after processing, see Table 7.

Table 7: Surface electrical resistivity behaviour of coatings containing specified surfactant combinations present in both supercoat and underlayer

| Cationic Surfactant | Anionic Surfactant | Total wt.% (supercoat wt.%) surfactant complex | Total wt.% (Supercoat wt.%) CF ₃ SO ₃ Li | Log R 50% RH (15% RH Before Processing | Log R 50% RH (15% RH) After Processing |
|---------------------|--------------------|--|--|--|--|
| Ethoquad HT/25 | Triton X-200 | 2.1 (2.6) | - (-) | 9.5 (11.7) | 10.8 (11.1) |
| Ethoquad HT/25 | Triton X-200 | 2.1 (2.6) | 1.05 (1.3) | 9.8 (12.6) | 11.7 (13.5) |
| Ethoquad HT/25 | Sermul EA211 | 2.1 (2.6) | - (-) | 9.5 (11.2) | 10.3 (11.75) |
| Ethoquad HT/25 | Sermul EA211 | 2.1 (2.6) | 1.05 (1.3) | 10.0 (11.2) | 10.75 (12.05) |
| Ethoquad HT/25 | Sermul EA146 | 2.1 (2.6) | - (-) | 9.5 (10.9) | 9.7 (10.4) |
| Ethoquad HT/25 | Sermul EA146 | 2.1 (2.6) | 1.05 (1.3) | 9.8 (11.0) | 11.85 (13.4) |

5 Note: R denotes surface electrical resistivity measured in ohms/square at 20°C.

The surfactant level used is equivalent to 1.10g/m² dry coverage.

The triflate level, when used, is equivalent to 0.55g/m² dry coverage.

Claims:

1. A multilayer silver halide photographic material having an outermost hydrophilic colloid layer comprising a plurality of surface active agents characterised in
5 that the surface active agents comprise a combination of an anionic surface active agent and a cationic surface active agent wherein at least one of said agents comprises at least one polyoxyalkylene group, said combination being present in an amount to provide from
10 0.05 to 0.2 g/m² dry coverage, and wherein a layer adjacent the outermost layer contains a dye.
2. A material according to claim 1 wherein the hydrophilic colloid is gelatin.
3. A material according to claim 1 or claim 2
15 wherein the combination of cationic surface active agent and anionic surface active agent is present in an amount to provide from 0.1 to 0.15g/m² dry coverage.
4. A material according to any one of the preceding claims wherein the molar ratio of cationic to
20 anionic surface active agent is from 1:2 to 2:1.
5. A material according to any one of the preceding claims wherein both cationic and anionic surface active agents comprise at least one polyoxyalkylene group.
- 25 6. A material according to any one of the preceding claims wherein the cationic surface active agent is a quaternised ethoxylated amine.
7. A material according to any one of the preceding claims wherein the anionic surface active agent
30 is an ethoxylated phosphate, sulphate, sulphonate or sulphosuccinate.
8. A material according to any one of the preceding claims wherein the dye is an antihalation dye.

9. A material according to any one of the preceding claims wherein the dye is an acid group-containing dye or a salt thereof.



Application No: GB 9507023.1
Claims searched: 1-9

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Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): G2C(CC19H2,C386,C388)

Int Cl (Ed.6): G03C

Other:

Documents considered to be relevant:

| Category | Identity of document and relevant passage | Relevant to claims |
|----------|---|--------------------|
| X | GB1445407 (MMM)(pages 4-5,Exs) | 1 at least |
| X | GB1417915 (KODAK)(pages2,4 and 5,Exs) | " |
| X | GB1439402 (MMM)(page 3,Exs) | " |
| X,E | EP0650088A (KODAK)(whole doc) | " |
| X | EP0633496A (MMM)(pages 13-14,16,Exs) | " |

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